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CO_2 Capture by Cold Membrane Operation

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Abstract

Air Liquide is developing a cost effective hybrid CO_2 capture process based on sub-ambient temperature operation of a hollow fiber membrane in combination with cryogenic separation. These membranes, when operated at temperatures below -20˚C, show two to four times increase in CO_2/N_2 selectivity with minimal CO_2 permeance loss compared to ambient temperature values. Long term (6 month) bench-scale testing with CO_2/N_2 mixtures at sub-ambient conditions has verified the enhanced separation performance seen at lab scale translated to commercial membrane modules [1, 2].
A relatively high CO_2 capture rate is required to drive down the cost per tonne of captured CO_2 as it valorizes the cost of the flue gas pre-treatment and compression prior to the membrane unit. However, as the CO_2 recovery increases, the productivity of the membrane module decreases, thereby driving up the membrane system capital cost. The main reason for this is a "pinch effect": the CO_2 driving partial pressure differential across the membrane decreases as CO_2 recovery proceeds. Computational fluid dynamics modelling shows that this effect can be partially off-set by a sweep operation where a small fraction (<5%) of the N_2-enriched retentate gas is fed into the permeate chamber. Experimental measurements were made with a commercial 12" membrane module, as a function of CO_2 recovery, in both sweep and non-sweep (baseline) mode. At the desired 90% CO_2 recovery level, sweep operation resulted in 30% higher membrane productivity with negligible effect on permeate purity. This would result in 30% lower membrane system cost with negligible change in specific energy for CO_2 capture.
Bench-scale process optimization work with synthetic CO_2/N_2 mixtures is currently being performed within Air Liquide's Delaware Research & Technology Center, USA; this will be followed by field testing at the National Carbon Capture Center (Wilsonville, Alabama, USA) with pre-treated flue gas from air-fired coal combustion.

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Keywords: Membrane; sub-ambient; CO_2

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1. Introduction

Air Liquide is developing a cost effective hybrid CO_2 capture process based on sub-ambient temperature operation of a hollow fiber membrane in combination with cryogenic separation. The process is based on operation with well established commercial Air Liquide membranes used in more than 2000 installations world-wide. We have recently discovered that these membranes, when operated at temperatures below -20˚C, show two to four times increase in CO_2/N_2 selectivity with minimal CO_2 permeance loss compared to ambient temperature values. Thus operation at low temperatures provides an unprecedented combination of CO_2 permeance and selectivity. Long term (6 month) bench-scale testing with CO_2/N_2 mixtures at sub-ambient conditions verified the enhanced separation performance seen at lab scale translated to commercial membrane modules [1, 2].

Cold membrane operation has potential applications for CO_2 recovery from flue gases in both oxy- and air-fired cases. It is also applicable to both natural gas and coal combustion. A possible mid-term application is EOR in relatively remote areas with CO_2 recovery from the flue gas of air / natural gas fired steam generators. A very large future opportunity, targeted by US DOE through recent solicitations, is post-combustion technology to capture at least 90% of the CO_2 in the flue gas from an air-fired pulverized coal power plant with a CO_2 capture cost of < \$40/tonne. Attaining this target requires improvement in both the specific energy (kWh/tonne of CO_2 captured) and the system capital cost.

Air Liquide's hybrid post-combustion CO_2 capture process concept uses the highly selective cold membrane to provide efficient pre-concentration of CO_2 prior to CO_2 partial condensation in a liquefaction unit. The CO_2 enriched permeate stream from the membrane is re-compressed, cooled in a heat exchanger and undergoes phase separation in the cryo-phase separator. Liquid CO_2 is pumped from the separator to provide an EOR or sequestration-ready product CO_2 at > 60 bar and 20°C. Recycling the incondensable gases from the liquefier back to the membrane creates a true hybrid solution. The process scheme shown in Figure 1 has been discussed previously [1, 2].

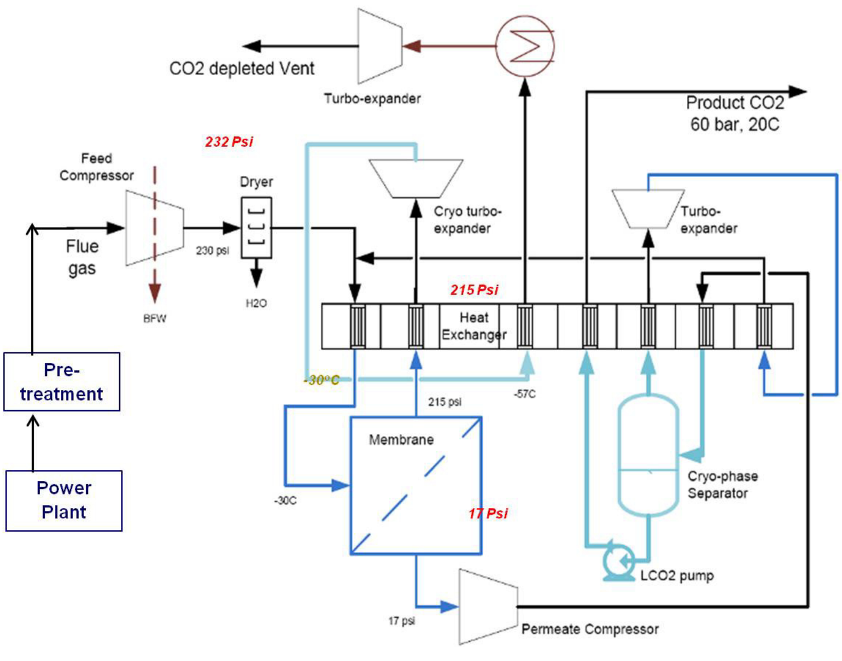

Figure 1. Schematic diagram of proposed membrane-based CO_2 CPU process

A relatively high CO_2 capture rate is required to drive down the cost per tonne of captured CO_2 as it valorizes the cost of the flue gas pre-treatment and compression prior to the membrane unit. However, bench-scale testing shows that as the CO_2 recovery increases, the productivity of the membrane module decreases, thereby driving up the membrane system capital cost. The main reason for this is a "pinch effect"; the CO_2 driving partial pressure differential across the membrane decreases as CO_2 recovery proceeds. This effect can be partially off-set by a sweep operation where a small fraction (<5%) of the N_2-enriched retentate gas is bled into the permeate chamber. Air Liquide's counter-current hollow fiber membrane modules are conceptually well suited to sweep operation. Simulations and experimental work show that this approach can markedly reduce membrane area requirements at high CO_2 recovery with negligible additional energy penalty.

Bench-scale process optimization work with synthetic CO_2/N_2 mixtures is currently being performed within Air Liquide's Delaware Research & Technology Center, USA; this will be followed by field testing at the National Carbon Capture Center (Wilsonville, Alabama, USA) with pre-treated flue gas from air-fired coal combustion. The current development work is supported by the Department of Energy National Energy Technology Laboratory under Award Number DE-FE0013163 (J. Figueroa, Program Manager).

Nomenclature

CPU	cryogenic purification unit
CFD	computer fluid dynamics
HF	hollow fiber

2. CO_2 separation by hollow fiber membrane modules

The hollow fiber (HF) membrane module configuration used by Air Liquide is a very economic configuration in terms of cost/membrane area. Due to the small hollow fiber size and the module construction method, commercial AL hollow fiber modules have an order of magnitude advantage in packing density (membrane area /module volume) over competing spiral wound configurations and an even greater advantage over plate and frame membranes.

The HF module is a shell and tube construction (Figure 2), with feed gas flowing through the bore of the fiber. CO_2 permeates through the fiber into the shell (permeate) space from where a CO_2 enriched stream is withdrawn for a permeate port. Elastomeric seals within the membrane vessel isolate the high pressure feed side from the low pressure permeate side. As CO_2 permeates along the axial length of the fibers, the CO_2 depleted / N_2 enriched retentate gas exits the vessel through the retentate port. At any point along the module the permeating flux J_i (moles of component i per unit area) is represented by

$$J_i = (\mathrm{P}/l)(p_h\, x_i - p_l y_i) \qquad (1)$$

where (P/l) is the permeance of component i, p_h and p_l are the feed (high) and permeate (low) side pressures and x_i and y_i are the feed and permeate side mole fractions of component i. The second bracketed term in eqn (1) represents the local partial pressure difference; this is the driving force for component i to permeate.

The counter-current arrangement of feed and permeate flows is an important aspect of this design as this configuration maximizes the partial pressure difference across the membrane. Counter current designs typically can have 20-50% higher module productivity than a cross-flow module with the same fiber intrinsic permeance-selectivity.

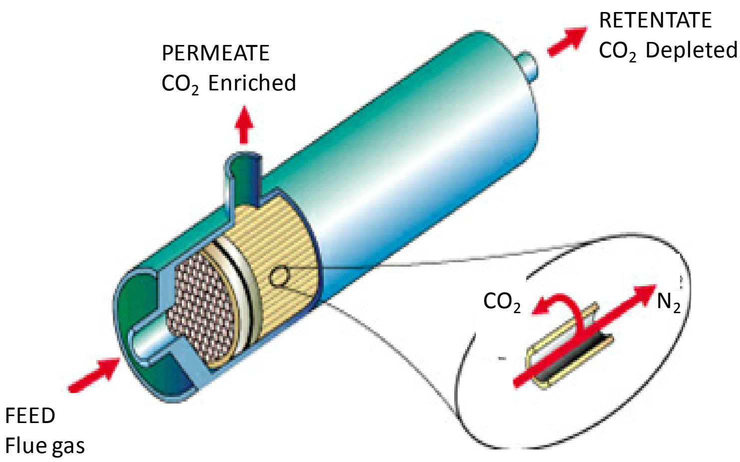

Figure 2. Air Liquide hollow-fiber membrane module for gas separation operating in counter-current flow configuration. Inset shows feed flow through the bore of a single fiber with fast gas CO_2 being enriched in permeate and N_2 enriched in retentate stream.

3. Simulation studies of sweep operation

As shown in eqn (1), the driving force for CO_2 permeation is the local difference in its partial pressure from feed to permeate side. As feed gas flows along the module length, the CO_2 concentration decreases, leading to a "pinch" in the partial pressure difference. This effect becomes particularly important for high CO_2 recovery, $\Re$, defined as:

$$\Re = Py_{CO2} / Fx_{CO2} \tag{2}$$

where P is the total permeate flow with composition y_{CO2} and F is the feed flow entering the module with composition x_{CO2}.

A computational fluid dynamics (CFD) model of a bore side feed membrane module was developed. The CFD model allows visualization of the predicted flow, concentration and pressure profiles flows and identification of any deviation from ideal behaviour. In this CFD study, the membrane module is modelled as two separate domains corresponding to the permeate stream and residue stream. Generally, the pressure drop can be modelled using Darcy's law with the pressure drop proportional to flow velocity for laminar flow. For the feed / retentate stream (bore side flow) pressure drop was calculated via the Hagen-Poiseuille equation. For the permeate stream (shell side flow), the longitudinal pressure drop along the membrane fibers was calculated via the Ergun equation. The (radial) pressure resistance across the membrane fibers was derived via the asymptotic model developed by Bruschke and Advani [3] with heterogeneous correction by T. Sadiq et al [4].

Figures 3 and 4 show simulation results from a 2-dimensional axisymmetric CFD model of the HF module. Figure 3 shows the simulation for baseline (no-sweep) configuration while Figure 4 shows the case with 2.5% sweep rate (% of the retentate flow). The simulation assumed intrinsic fiber permeance as the values measured in minipermeators at the feed conditions of 15 bar and -40C. The feed flow, pressure and temperature in both simulations were constant.

Figure 3 shows two important performance aspects:

(i) most of the CO_2 in the permeate is transported relatively close to the feed end;

(ii) the remaining fiber length permeates less moles of CO_2 because of the low driving force but is required to achieve high CO_2 recovery.

These performance aspects are the impetus for the sweep configuration shown in Figure 4. A small fraction of the retentate stream is diverted, expanded and added to the permeate domain. Comparing the sweep simulation shown in Figure 4 with the baseline case in Figure 3, shows that the driving force for CO_2 permeation at the feed end is negligibly affected; hence the overall permeate purity is minimally decreased. However at the retentate end, the driving force is improved so that more of the module operates at higher rates of CO_2 permeation.

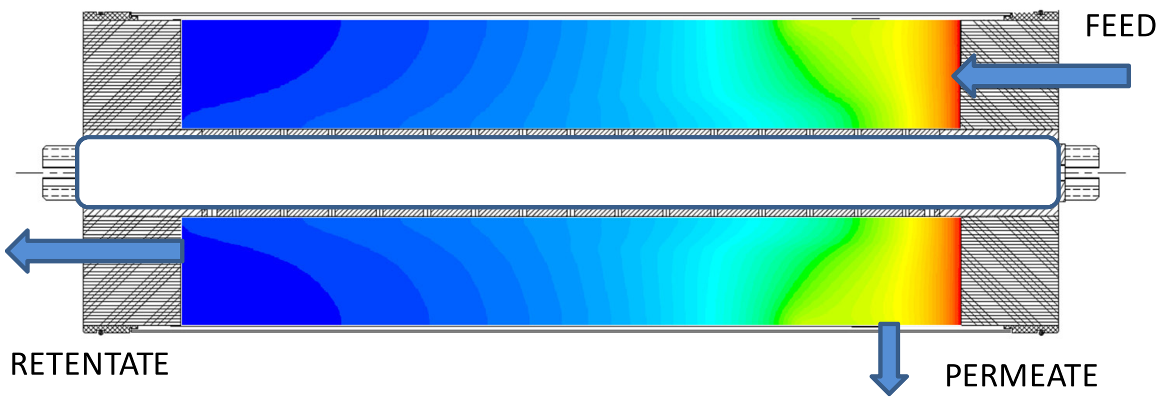

Figure 3. No-sweep case. 2-D axisymmetric CFD simulation of Air Liquide hollow-fiber membrane module showing the CO_2 partial pressure difference along the module axial length. The partial pressure difference is color coded with the warmest colors (red) indicating the highest values and blue indicating the lower values.

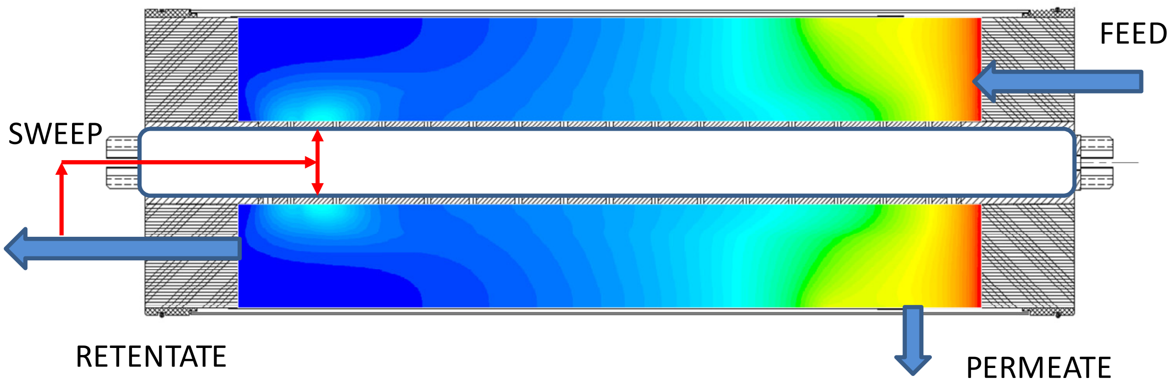

Figure 4. 2.5% Sweep case. 2-D axisymmetric CFD simulation of Air Liquide hollow-fiber membrane module showing the CO_2 partial pressure difference along the module axial length. The partial pressure difference color code is the same as Figure 3.

Addition of a sweep stream to a module changes the permeate side concentration distribution. In this case, as indicated in Figure 4, we studied diverting a small fraction of the CO_2 depleted retentate stream to sweep the permeate side, flowing counter-current to the feed. The main effect of the sweep is to dilute the permeate concentration of the faster gas, especially at the process-limiting retentate end. Lowering the partial pressure of the fast gas (CO_2) and increasing the partial pressure of the slower gas (N_2) in the permeate at the retentate end increases the local driving force, thus mitigating the pinch effect for CO_2 in the last ~ 30% of the module. The concentrations of the intermediate permeance gas (O_2) are relatively flat. Since the sweep effect is mainly confined to the retentate end, it is fundamentally different than simply operating at lower membrane selectivity. The predicted permeate side concentration profiles, with and without sweep are shown in Figure 5.

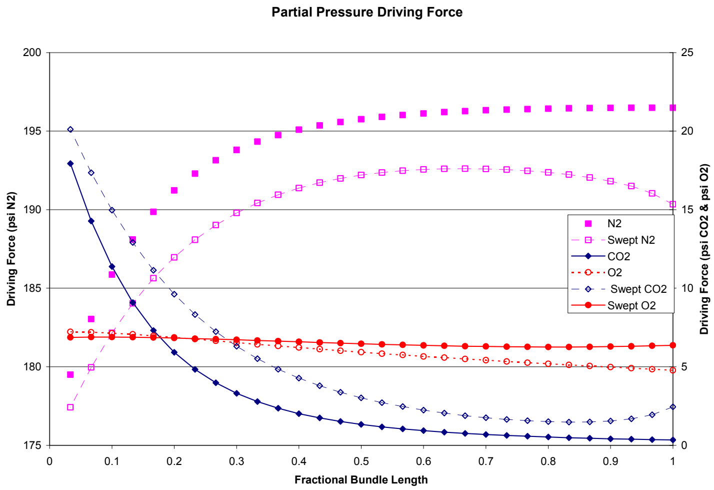

Figure 5. Plots of CO_2, O_2 and N_2 partial pressure driving force along the module axial length. The feed entry is at length = 0.

Figure 6 shows that at a given recovery, module productivity increases and correspondingly the required membrane area for a given feed flow decreases monotonically as sweep rate increases. However, addition of any amount of sweep will reduce CO_2 concentration in the permeate. The permeate volume is also increased, ultimately requiring more recycle (see Figure 1). Lower permeate concentration reduces the liquefier efficiency and would be expected to result in higher specific energy requirements for overall CO_2 capture. However, as shown in Figure 6 this effect is predicted to be negligible at low sweep rates (< 5% of the retentate flow). This insensitivity to small sweep rates is due to the severe pinching at high CO_2 recovery. At yet higher sweep rates, as the CO_2 permeate concentration begins to decrease noticeably, the increasing flow rate of incondensables to the liquefier will decrease overall process performance. However, since the change in permeate CO_2 concentration is small up to 5% sweep rate, the specific energy for CO_2 capture is also relatively constant until this point.

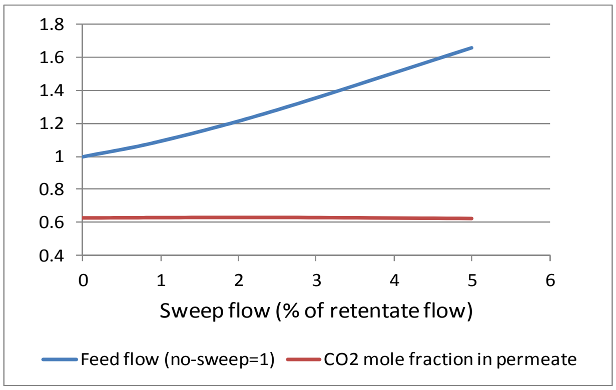

Figure 6. Predicted plots of CO_2 concentration in permeate and relative feed flow through a single module operating at 90% CO_2 recovery with sweep rates from 0-5% of retentate flow..

4. Experimental validation of sweep operation

A commercial 12” membrane module and vessel were modified for sweep operation. The module retentate line was tapped for withdrawing a small sweep stream through an expansion valve. The sweep flow rate was set by a flow controller. The sweep flow was introduced into the shell side (permeate side) at the retentate end of the module through holes in the center core on which the membrane fibers are wrapped. The sweep thus flows in a counter-current manner, along with the permeate stream to the permeate withdrawal port located at the opposite (feed) end (see sweep schematic superimposed on CFD simulation in Figure 4).

Preliminary tests were conducted with sweep operation to validate the expected increase in membrane productivity [5]. Data was generated with a clean gas mixture simulating the main components of a coal plant flue gas. The feed gas mixture (18% CO_2, 5% O_2, balance N_2) was set as the expected feed composition to the membrane in the proposed cold membrane scheme (Figure 1). Because the scheme incorporates various CO_2 recycle streams, the membrane feed is higher in CO_2 than the incoming flue gas from the boiler.

The membrane was first operated in normal (no-sweep) mode to establish a baseline performance. A small amount (2 to 5%) of the retentate gas was then recycled to the module through an expansion valve / flow controller and used as sweep flow. The sweep flow arrangement was shown in Figure 4. This resulted in a significant improvement in the module productivity, as shown in Figure 7.

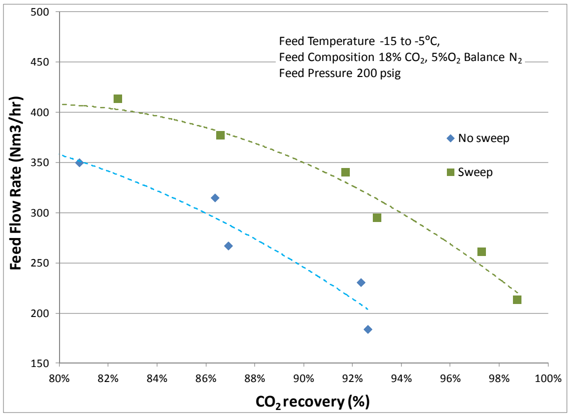

Figure 7. Plots of feed flow through a module as a function of CO_2 recovery for baseline (no sweep) and 2-5% sweep operation.

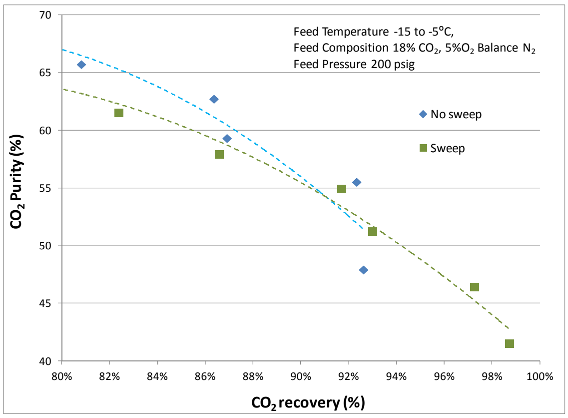

Figure 8. Plots of CO_2 concentration in permeate through a module as a function of CO_2 recovery for baseline (no sweep) and 2-5% sweep operation.

Figure 7 shows that for any given CO_2 recovery, the feed flow through the membrane module with sweep is higher than the baseline case. The difference in membrane productivity between sweep and baseline operation increases as CO_2 recovery increases and pinch effects become more important. At 90% CO_2 recovery, the feed flow with sweep was increased by 30% relative to the baseline case. This productivity improvement corresponds directly to decreased membrane capital cost requirement.

The corresponding Figure 8 shows the CO_2 permeate concentration also as a function of CO_2 recovery. Though we saw a large 30% improvement in module productivity in Figure 7, Figure 8 shows that there is negligible change in the CO_2 purity between sweep and baseline operation for the low sweep rates chosen. This will result in essentially unchanged specific energy CO_2 with sweep operation, even though the process capital cost will be significantly reduced.

5. Conclusions

A relatively high CO_2 capture rate is required to drive down the cost per tonne of captured CO_2 as it valorizes the cost of the flue gas pre-treatment and compression prior to the membrane unit. However, bench-scale testing shows that as the CO_2 recovery increases, the productivity of the membrane module decreases, thereby driving up the membrane system capital cost. We have demonstrated through both CFD modelling as well as experimentally that membrane sweep operation can be used to reduce this cost. Sweep operation with a commercial 12” membrane module resulted in 30% higher membrane productivity with negligible effect on permeate purity. This would result in 30% lower membrane system cost with negligible change in specific energy for CO_2 capture.

Acknowledgements

The current development work [5] is supported by the Department of Energy National Energy Technology Laboratory under Award Number DE-FE0013163 (J. Figueroa, Program Manager).

References

[1] S.S. Kulkarni et al, CO_2 capture by sub-ambient membrane operation, 2012 NETL CO_2 Capture Technology Meeting, July 9 - 12, 2012. NETL Award # DE-FE0004278

[2] D.J Hasse et al, CO2 capture by sub-ambient membrane operation, Energy Procedia, Volume 37, Pages 993–1003, 2013, (presented at GHGT-11)

[3] M.V. Bruschke, and S.G. Advani, Flow of generalized Newtonian fluids across a periodic array of cylinders, Journal of Rheology, 37, 479-498, 1992

[4] T.A.K. Sadiq et al, Experimental investigation of transverse flow through aligned cylinders, Int. J. Multiphase Flow. Vol. 21, No. 5, pp. 755-774, 1995

[5] T Chaubey et al, CO_2 capture by cold membrane operation with actual coal fired power plant flue gas, 2014 NETL CO_2 Capture Technology Meeting, July 31, 2014. NETL Award # DE-FE0013163